Structure and Thermophysical Properties of Fullerene C_{60} Aqueous Solution[1]

Yu.I. Prylutskyy[2], S.S. Durov[2], L.A. Bulavin[2], I.I. Adamenko[2], K.O. Moroz[2],

I.I. Geru[3], I.N. Dihor[3], P. Scharff[4], P.C. Eklund[5], L. Grigorian[5]

---

[1]Paper presented at the Fourtheenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A.

[2]Dept. of Physics, Kyiv National Shevchenko University, Volodymyrska Str., 64, 01033 Kyiv, Ukraine

[3]Dept. of Physics, State University of Moldova, Chisinau MD 009, Moldova

[4]Institute of Physics, TU Ilmenau, PF 100565, D-98684 Ilmenau, Germany

[5]Dept. of Physics, Penn State University, University Park, PA 16802-6300, U.S.A.

[2]Yu.I. Prylutskyy, Dept. of Physics, Kyiv National Shevchenko University, Volodymyrska Str., 64, 01033 Kyiv, Ukraine (E-mail: prilut@office.ups.kiev.ua)

ABSTRACT

The structure and thermophysical properties of fullerene C_{60} aqueous solution were investigated both experimentally and theoretically in detail. The aggregation kinetics results indicated that the structure of fullerene C_{60} aggregates in water could be described as a fractal system. The IR and electronic absorption spectra obtained confirm the presence of the crystalline phase in aqueous solution. The numerical values of thermodynamical coefficients α_P, β_T, β_S, c_P, c_V and sound velocity were determined from the (P-V-T) data measured. The vibrational spectrum of crystalline structure (T_h symmetry group) formed from the hydrated single fullerene C_{60} molecules in aqueous solution was calculated using the molecular dynamics approach.

KEY WORDS: fullerene C_{60} aqueous solution; IR and electronic absorption spectra; molecular dynamics approach; thermophysical properties.

1. INTRODUCTION

Fullerenes are widely investigated currently and have potential for various technical applications [1]. In particular for biomedical testing, water-soluble forms of fullerenes are undoubtedly of great interest. Recently Andrievsky and co-workers [2,3,4] proposed a method for obtaining aqueous solutions of fullerene C_{60} without any stabilizers and chemical modification. These dark brownish-orange fullerene C_{60} water solutions are stable during (12-18) months and more on storage at the normal conditions $(4\text{-}40)^0$ C. The maximum reached concentration of fullerene C_{60} in the water solution is approximately equal 2.3 $g \cdot l^{-1}$(for comparison, the solubilities C_{60} are 1.7 $g \cdot l^{-1}$and 2.9 $g \cdot l^{-1}$in benzene and toluene, respectively). The fullerene C_{60} aqueous solutions are shown to be the ultramicroheterogeneous and polydisperse systems containing the spherical C_{60} aggregates (both single fullerene C_{60} molecules and their fractal clusters with diameter from 3.4 to 36 nm) in a hydrated state (i.e., the fullerene aggregates are covered by a strong hydrated shell). Moreover, the crystalline phase, experimentally observed in the fullerene C_{60} aqueous solution, consists of sphere-shaped C_{60} aggregates of (1-4) nm size. Hence more detailed theoretical and experimental studies of the structure, vibrational and thermodynamical properties of the fullerene C_{60} aqueous solution are important.

2. THEORY AND EXPERIMENT

2.1. Study of structure of fullerene C_{60} clusters in aqueous solution

Let us assume that the formation of clathrate-like networks of water molecules around fullerene C_{60} aggregates, stabilized due to the 1ow conformational mobility of fullerenes and geometrical matching between the structures, which may be formed by

hydrogen bonding of water molecules in the clathrate and covalent bonds of the fullerene carbon atoms takes place [2,3,4].

The free energy of the system "fullerene C_{60} cluster + aqueous solution" at the temperature T includes the following contributions

$$E = U_1 + U_2 + U_3 - T\Delta S, \qquad (1)$$

where: (1) <u>within the cluster</u>: a Lennard-Jones (12-6) atom-atom potential and electrostatic potential of charges located on single and double bonds of the C_{60} molecule:

$$U_1 = \sum_{\mu,\mu'} \left\{ 4\varepsilon \sum_{i,j} \left[\left(\frac{\sigma}{|\mathbf{r}_{\mu i} - \mathbf{r}_{\mu' j}|} \right)^{12} - \left(\frac{\sigma}{|\mathbf{r}_{\mu i} - \mathbf{r}_{\mu' j}|} \right)^{6} \right] + \sum_{m,n} \frac{q_m q_n}{|\mathbf{r}_{\mu m} - \mathbf{r}_{\mu' n}|} \right\}. \qquad (2)$$

Here $r_{\mu i}$ and $r_{\mu m}$ are the coordinates of the i-th carbon atom and m-th bond center in the molecule μ, respectively; q_m is the effective charge of the m-th bond and equals q in the case of a single bond and -2q for a double bond. The values of the parameters ε, σ and q were taken from our previous paper on the simulation of the solid C_{60} structure [5];

(2) <u>within the water medium</u>: a dipole-dipole interaction of water molecules (the first coordination sphere):

$$U_2 = \sum_{\nu,\nu'} \left\{ \frac{\mathbf{d}_\nu \cdot \mathbf{d}_{\nu'}}{r^3_{\nu\nu'}} - \frac{3(\mathbf{d}_\nu \cdot \mathbf{r}_{\nu\nu'})(\mathbf{d}_{\nu'} \cdot \mathbf{r}_{\nu\nu'})}{r^5_{\nu\nu'}} \right\}. \qquad (3)$$

Here d_ν=1.6 D is the dipole moment of single water molecule ν;

(3) <u>outside the cluster</u>: a polarization interaction of each C_{60} molecule in the cluster with the water medium:

$$U_3 = -\alpha \sum_{\nu,\nu'} \frac{d_\nu^2\left(\theta_{\nu,\nu'}\right)}{r_{\nu\nu'}^6}. \qquad (4)$$

Here $\alpha=8.48\times10^{-2}$ nm^3 is the polarizability of single fullerene C_{60} [6] and $\theta_{\nu\nu'}$ is the angle between the dipole moments of water molecules ν and ν′;

(4) The isothermal change of the entropy ΔS for the system "fullerene C_{60} cluster + aqueous solution" has been calculated by the formula:

$$\Delta S = -\int \left(\frac{\partial V}{\partial T}\right)_P dP. \qquad (5)$$

The results obtained are shown in Fig. 1.

The minimization of the free energy (1) was perfomed by using the dense-packing principle. The calculated energy (normalized to one molecule) of possible hydrated $(C_{60})_N$ clusters plotted against a number of single molecules C_{60} entering in them is shown in Fig. 2. As can be seen the smallest stable fullerene C_{60} cluster (I_h symmetry group) consists of 13 C_{60} molecules. Its diameter is equal to 3.36 nm (with accounting of molecular diameter of the water molecule ~ 0.28 nm [7,8]). This result is in excellent agreement with the scanning tunneling microscopy data [3,4], which confirm that the smallest stable spherical clusters in the fullerene C_{60} aqueous solution have a mean size equal to 3.4 nm. Other clusters presented in Fig. 2 are stable (the numbered clusters) or partly stable (the un-numbered clusters) in aqueous solution.

Let us remember that without stresses of valency angles, the diameter of the shell formed from the water molecules around the dissolved aggregate can be increased to 2 nm [7], and within the admissible stresses of hydrogen bonds can be increased even to 6 nm [8]. The results obtained for the stable fullerene $(C_{60})_N$ clusters with a number

of molecules 13≤N≤120 do not contradict this fact. On the other hand, it is known [9] that the water has a cluster structure and the diameter of these clusters is 10 nm. The size of the $(C_{60})_N$ clusters with a number of molecules 13≤N≤239 does not exceed this value. Hence the fullerene C_{60} aqueous solution may combine some properties of a typical colloidal solution with those of a true molecular solution.

2.2. Study of aggregation of fullerene C_{60} in aqueous solution

According to the fractal concept [10] two limiting regimes of irreversible colloids, namely reaction limited cluster aggregation (RLCA) (a slow aggregation process) and diffusion limited cluster aggregation (DLCA) (a fast aggregation process), have been used to characterize the structure and kinetics of colloidal fractal aggregates. The fractal dimension d_f is approximately equal to 2.1 for RLCA, which exhibits exponential kinetics, $M \sim e^{Bt}$, where M and B are the average mass of the cluster and a constant, respectively. For DLCA, $d_f \approx 1.8$ and M increases linearly with time.

The increase of the average molar mass M as a function of aggregation time is shown in Fig. 3. As can be seen, the linear dependence obtained (the continuous curve in Fig. 3) reflects the fast aggregation process directly (i.e., DLCA case).

According to the DLCA theory, the relationship between the number of particles in a cluster (N), its radius (R) and its fractal dimensionality (d_f) has the form [10]

$$N=\left(\frac{R}{r}\right)^{d_f}, \qquad (6)$$

where r is the radius of a particle forming the cluster. In accordance with Eq. (6) and with the values N=13, R=1.4 nm (the radius of the smallest stable $(C_{60})_{13}$ cluster without accounting of molecular diameter of the water molecule) and r=0.35 nm (the radius of a

single C_{60} molecule [11]) we found that $d_f \approx 1.85$, which confirms the above experimental result ($d_f \approx 1.8$).

By analyzing the sizes of the observed fullerene C_{60} spherical particles in water, Andrievsky and co-workers [3,4] revealed that their diameters regularly rise within the range from 3.4 to 36 nm and are equal to 3.4, 7.1, 10.9, 14.5, 18.1, 21.8, 25.4, 28.8, 32.4 and 36.0 nm. Taking the smallest hydrated spherical $(C_{60})_{13}$ cluster with diameter of 3.4 nm (3.36 nm according to our theoretical calculations) as the first member, we can see that each following particle is larger than the preceding one by (3.4-3.8) nm. Note that the regularity found for the observed sphere-shaped particles will be valid only if the cluster of size 3.4 nm is taken as the primary one. Hence one can assume that the above row of fullerene C_{60} particles should be formed of hydrated $(C_{60})_{13}$ cluster.

2.3. Study of optical spectra of fullerene C_{60} aggregates in aqueous solution

According to one-electron model, the C_{60} molecule ground state consists of five occupied orbital states (HOMO) of h_u symmetry, each having doubly spin degeneration [12]. The lowest not occupied molecular orbitals are three t_{1u} symmetry doubly spin degenerated states (LUMO). One-electron electric dipole $h_u \leftrightarrow t_{1u}$ transitions (HOMO$\leftrightarrow$ LUMO) with the photons absorption or emission are forbidden due to the same parity (respective wave functions are odd) of the orbital states. The first allowed dipole transition, corresponding to minimum excitation energy of molecule C_{60} is $h_u \leftrightarrow t_{1g}$ (HOMO$\leftrightarrow$"LUMO+1 state"). Dipole allowed transitions in order of the molecule excitation energy increasing, are the following: $(h_g+g_g) \leftrightarrow t_{1u}$ (HOMO–1$\leftrightarrow$LUMO), $h_u \leftrightarrow h_g$ (HOMO$\leftrightarrow$LUMO+3) and $(h_g+g_g) \leftrightarrow t_{2u}$ (HOMO–1$\leftrightarrow$LUMO+2) [1]. Interactions between C_{60} molecules in fluid ambience and in the fullerite do not significantly change the molecular orbitals electronic wave functions [13,14]. Therefore, the structure of

electronic spectrum of free molecules C_{60} and fullerene molecules in fluid or in crystalline state must differ slightly. Herewith, the transition from the molecules non-interacting state to condensed ones is accompanied by the small shifts of lines in the optical spectrum and their widening. This is experimentally confirmed. The fullerene C_{60} aggregates in water spectral absorption coefficient dependence in the UV-VIS range (1.6-6.2) eV is shown in Fig. 4. Four intensive lines of absorption with maximums at 2.92, 3.62, 4.66 and 5.63 eV are related to dipole allowed transitions specified above. The positions of these lines are in good agreement with the data of ellipsometric and optical transparency measurements for crystalline C_{60} [6,15,16,17,18]. Besides, in accordance with the above mentioned, the UV-VIS absorption spectrum of fullerite nanostructure differs insignificantly from C_{60} molecules spectrum in n-hexane (3.7, 4,6 and 5.8 eV [6]) or in decaline (~3, 3.6, 4.7 and 5.7 eV [19]). The half-widths of lines with maximum at 3.62, 4.66 and 5.63 eV are in the interval of (0.25-0.66) eV, but the line with maximum at 2.92 eV has the width ~0.05 eV. The line of low intensity caused by optical dipolar-forbidden transition $h_u \leftrightarrow t_{1u}$ (Fig. 4) is also observed in the range of fundamental absorption edge (~2 eV). Thus, the dipole forbidden optical transitions at the photons energy increasing turn into to dipolar-allowed optical transitions with simultaneously increasing of absorption lines intensities. Indeed, in the case of optical transition the square of the matrix element of the dipole momentum operator between initial and final states is a function of photons energy.

Though the electronic spectra of fullerene C_{60} molecules in fluid and crystalline states differ insignificantly, the fact of presence in water of fullerite nanostructure can be experimentally determined in optical spectra. For this, it is necessary to prove the existence of indirect optical transitions, which are typical for crystalline state. The

spectral profiles of direct allowed, indirect allowed and indirect forbidden transitions are obtained from the absorption spectrum of Fig. 4 according to dependence $(E\cdot\alpha)_\gamma=f(E)$, where α is absorption coefficient, E is energy of photons and γ=2/3, 2, 1/2 and 1/3 for direct forbidden, direct allowed, indirect allowed and indirect forbidden transitions, respectively. This treatment, as is well known, is used in theory of semiconductors for determination of optical transition type. The existence of the direct allowed optical transitions ($h_u\leftrightarrow t_{1g}$, $(h_g+g_g)\leftrightarrow t_{1u}$, $h_u\leftrightarrow h_g$, $(h_g+g_g)\leftrightarrow t_{2u}$), indirect allowed optical transitions ($h_u\leftrightarrow t_{1g}$, $(h_g+g_g)\leftrightarrow t_{1u}$) and indirect forbidden optical transitions ($h_u\leftrightarrow t_{1g}$, $(h_g+g_g)\leftrightarrow t_{1u}$) in the fullerene C_{60} aggregates in water is shown in Fig. 5 and Fig. 6. The E_g values for direct and indirect dipole forbidden and dipole allowed transitions, as well as phonons energy, of the indirect optical transitions, are given in Table I. The γ index in Table I indicates the $(E\cdot\alpha)$ product degree in $(E\cdot\alpha)_\gamma=f(E)$ dependence. We shall note that in Table I the transition types are marked with the same symbols $h_u\leftrightarrow t_{1g}$ and $(h_g+g_g)\leftrightarrow t_{1u}$ both for direct and indirect transitions respectively. Truly, the final state of indirect transition corresponds to wave vector $\mathbf{k}=\mathbf{k}_0\neq 0$ and it is transformed as the irreducible representation of the wave vector $G_{\mathbf{k}0}$ group. The final state symmetries for two specified types of indirect transition should be elucidated. We shall mention also that in the case of indirect forbidden transition $(h_g+g_g)\leftrightarrow t_{1u}$ the energy of phonon E_{ph}=1900.0 cm^{-1} exceeds the limiting energy for "intern" phonons of the fullerite C_{60}. It is possible that two phonons with summary energy equal to 1900.0 cm^{-1} participate in this transition.

Thus, the structure and the parameters of electronic spectrum (Fig. 4,5,6 and Table I) indicate the presence of fullerene C_{60} molecules in the investigated liquid. The

revealed indirect optical transitions in this case unequivocal prove the existence of the crystalline state of fullerene molecules, as fullerene C_{60} aggregates in aqueous solution.

2.4. Study of vibrational spectrum of fullerene C_{60} crystal in aqueous solution

Earlier we found [20] that the values of vibrational Raman frequencies of the fullerene C_{60} aqueous solution increase in comparison with results for individual C_{60} molecules [21] by the magnitude of (2-6) per cents. This increase we associate with strengthening the intramolecular bonds on forming hydrated fullerene C_{60} aggregates in aqueous solution described above. In other words the effect of water comes to external hydrostatic compression of the molecules C_{60} in the aggregate leading to the negligible decrease of its geometrical sizes and increase of bond energy.

As known C_{60} molecules freely rotate in the solid at room temperature [22]. In our opinion, the effect of water on the forming crystal structures is connected with the fixation of hydrated C_{60} molecules orientation in the unit cell of the lattice (i.e., the transition from disordered structure to orientationally ordered crystalline phase [23] takes place). Thus, we shall be consider the following structure of solid C_{60} in aqueous solution: the number of hydrated C_{60} molecules in the unit cell is Z=4, the space group is T_h and the lattice constant is a=1.85 nm (for comparison, a=1.40 nm for solid C_{60} [23]).

The minimization of the free energy of C_{60} crystal in aqueous solution

$$E= U_1 + U_2 + U_3 \qquad (7)$$

was perfomed by using the atom-atom potential method described in detail in our previous paper [24]. In particular, it was found that the minimum of the lattice energy for solid C_{60} in aqueous solution equals E_{min}=-2.5 eV (for comparison, E_{min}=-1.9 eV for solid C_{60} [24]).

The values of fundamental intermolecular frequencies of C_{60} crystal in aqueous solution in the center of the Brillouin zone (**k**=0) were calculated based on the analytical formulas [24]. The results obtained are represented in Table II. It is seen that the calculated vibrational frequencies for C_{60} crystal in aqueous solution are located lower than the calculated fundamental modes for solid C_{60} [24]. All g-modes are Raman active and only two F_u modes are IR active. The theoretical values are different from the experimental data obtained for the IR modes by up to 11 per cents.

2.5. Study of thermophysical properties of fullerene C_{60} aqueous solution

The (P-V-T) data of fullerene C_{60} aqueous solution were measured by use the metallic bellow method with differential inductive sensor of linear shifts in the temperature range of (295-310) K and pressure range of (0.1-153) MPa. As a result we found the numerical values for the isobaric coefficient of thermal expansion - $\alpha_P=4.0\times10^{-4}$ K^{-1}, for the isothermal compressibility - $\beta_T=2.2\times10^{-4}$ MPa^{-1} (for comparison, $\beta_T=4.7\times10^{-4}$ MPa^{-1} for water) and for the molar heat capacity - $c_P=75.5$ $J\cdot mol^{-1}\cdot K^{-1}$ under ambient conditions.

The value of adiabatic compressibility coefficient β_S was calculated from following formula [25]

$$c_P = \frac{\alpha_P^2 T}{\rho(\beta_T - \beta_S)}, \qquad (8)$$

where $\rho=1754$ $kg\cdot m^{-3}$ is the density of fullerene C_{60} aqueous solution at room temperature. Note that on the liquid-vapor equilibrium line the density was measured using the bottle method. It turned out that $\beta_S=1.76\times10^{-4}$ MPa^{-1} under ambient conditions.

Finally, the values of molar heat capacity c_V and sound velocity v_S were found from the formulas [25]:

$$\beta_S = \frac{1}{\rho v_S^2}, \tag{9}$$

$$c_V = c_P \frac{\beta_S}{\beta_T}. \tag{10}$$

It turned out that v_S=1.8 $km \cdot s^{-1}$ (for comparison, v_S=1.5 $km \cdot s^{-1}$ for water) and c_V=60.4 $J \cdot mol^{-1} \cdot K^{-1}$ under ambient conditions.

3. RESULTS

We have demonstrated that the fullerene C_{60} in aqueous solution could aggregate rapidly at room temperature. The kinetic study showed that the structure of C_{60} aggregates could be described as a fractal with a dimension of (1.8-1.85). The hydrated spherical cluster (I_h symmetry group) with diameter of 3.36 nm containing 13 molecules C_{60} was shown to be the smallest stable form among all the possible aggregates. By analyzing the sizes of the observed fullerene C_{60} spherical particles in aqueous solution [3,4] we found that these aggregates should be formed of hydrated $(C_{60})_{13}$ cluster. The optical absorption spectra of C_{60} aqueous solution testify to the crystalline character of absorption. The calculated intermolecular spectrum of C_{60} crystal (T_h symmetry group) in aqueous solution was found to be in satisfactory agreement with IR spectroscopy data. The thermophysical characteristics (α_P, β_T, β_S, c_P, c_V and sound velocity) of fullerene C_{60} aqueous solution were determined.

ACKNOWLEDGMENTS

This research work was supported by the CR NATO grant. The authors thank Dr. G.V. Andrievsky for kindly providing of fullerene C_{60} aqueous solution.

REFERENCES

1. M.S. Dresselhaus, G. Dresselhaus and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, New York, 1996).
2. N.O. Mchedlov-Petrosyan, V.K. Klochkov and G.V. Andrievsky**,** *J.Chem.Soc., Faraday Trans.* **93:** 4343 (1997).
3. G.V. Andrievsky, V.K. Klochkov, E.L. Karyakina and N.O. Mchedlov-Petrosyan, *Chem.Phys.Lett*. **300:** 392 (1999).
4. G.V. Andrievsky, V.K. Klochkov and L.I. Derevyachenko, 4th Biennial International Workshop in Russia: *Fullerenes and Atomic Clusters*, St.-Petersburg, 1999, Abstracts of Invited Lectures and Contributed Papers, p. 169.
5. Yu.I. Prilutski, E.V. Buzaneva, L.A. Bulavin and P. Scharff, *Carbon* **37:** 835 (1999).
6. S.L.Ren, Y. Wang, A.M. Rao, E. McRae, J.M. Holden, T. Hager, K. Wang, W.T. Lee, J. Selegue and P.C. Eklund, *Appl. Phys. Lett.* **59:** 2678 (1991).
7. S.P. Gabuda, *Combined Water. Facts and Hypotheses* (Nauka, Novosibirsk, 1982).
8. S. Wei and A.W. Castlemann, *Int.J. Mass Spectr. Ion Process*. **131:** 233 (1994).
9. G.V. Yukhnevich and V.V. Volkov, *Dokl.Akad.Nauk* **353:** 465 (1997).
10. B.M. Smirnov, *Physics of Fractal Aggregates* (Nauka, Moscow, 1991).
11. H.W. Kroto, J.R. Health, S.C. O'Brein, R.F. Curl and R.E. Smalley, *Nature* **318:** 162 (1985).
12. R.C. Haddon, *Acc. Chem. Res***. 25:** 127 (1992).
13. S. Saito, S. Sawada and R. Zanasi, *Chem. Phys. Rev. B.* **45:** 6912 (1992).
14. C.H. Xu and G.E. Scuseria, *Phys. Rev. Lett***. 72:** 669 (1994).
15. G. Gensterblum, J.J. Pireaux, P.A. Thiry, R. Caudano, J.P. Vigneron, P. Lambin, A.A. Lucas and W. Kratschmer, *Phys. Rev. Lett.* **67:** 2171 (1991).

16. E. Sohmen and J. Fink, *Phys. Rev. B.* **47:** 14532 (1993).

17. S. Modesti, S.Gerasari and P. Rudolf, *Phys. Rev. Lett.* **71:** 2469 (1993).

18. V.I. Srdanov, C.H. Lee and N.S. Sariciftci, *Thin Sol. Films* **257:** 233 (1995).

19. S. Leach, M. Vervloet, A. Despres, E. Breheret, J.P. Hare, T.J. Dennis, H.W. Kroto and D.R.M. Walton, *Chem. Phys.* **160:** 451 (1992).

20. Yu.I. Prilutski, S.S. Durov, V.N. Yashchuk, T.Yu. Ogul'chansky, V.E. Pogorelov, Yu.A. Astashkin, E.V. Buzaneva, Yu.D. Kirghizov, G.V. Andrievsky and P. Scharff, *Eur.Phys.J. D.* **9:** 341 (1999).

21. D.S. Bethune, G. Meijer, W.C. Tang, H.J. Rosen, W.G. Golden, H. Seki, C.A. Brown and M.S. de Vries, *Chem.Phys.Lett.* **179:** 181 (1991).

22. W. Kratschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature* **347:** 354 (1990).

23. W.I.F. David, R.M. Ibberson, J.C. Matthewman, K. Prassides, T.J.S. Dennis, J.P. Hare, H.W. Kroto, R. Taylor and D.R.M. Walton, *Nature* **353:** 147 (1991).

24. Yu.I. Prilutski and G.G. Shapovalov, *Phys.St.Sol.(b)* **201:** 361 (1997).

25. J.O. Hirschfelder, Ch.F. Curtiss and R.B. Bird, *Molecular theory of gases and liquids* (John Wiley and Sons, Inc., New York , 1954).

Table I. The energy gaps determined from direct and indirect optical transitions data for the fullerene C_{60} aggregates in aqueous solution

Type of transition	Direct forbidden	Direct allowed	Indirect allowed		Indirect forbidden	
	E_g, eV	E_g, eV	E_g, eV	E_{ph}, cm^{-1}	E_g, eV	E_{ph}, cm^{-1}
$h_u \leftrightarrow t_{1u}$	1.77	-	-	-	-	-
$h_u \leftrightarrow t_{1g}$	-	2.37	1.89	879.3	1.71	903.5
$(h_g+g_g) \leftrightarrow t_{1u}$	-	3.27	2.56	1097.1	2.14	1900.0
$h_u \leftrightarrow h_g$	-	4.02	-	-	-	-
$(h_g+g_g) \leftrightarrow t_{2u}$	-	4.90	-	-	-	-
γ	2/3	2	1/2		1/3	

Table II. Frequencies (in cm^{-1}) of intermolecular modes in the center of the Brillouin zone

Symmetry	solid C_{60} (theory [24])	crystal C_{60} in aqueous solution (theory)	crystal C_{60} in aqueous solution (experiment)
A_u	35.0	26.9	
E_u	46.7	35.9	
F_u	42.9	33.0	36.6
F_u	51.0	39.2	41.9
A_g	18.6	14.3	
E_g	18.5	14.2	
F_g	17.1	13.2	
F_g	17.5	13.5	
F_g	22.0	16.9	

FIGURE CAPTIONS

Fig. 1. Calculated isothermal change of the entropy for fullerene C_{60} aqueous solution

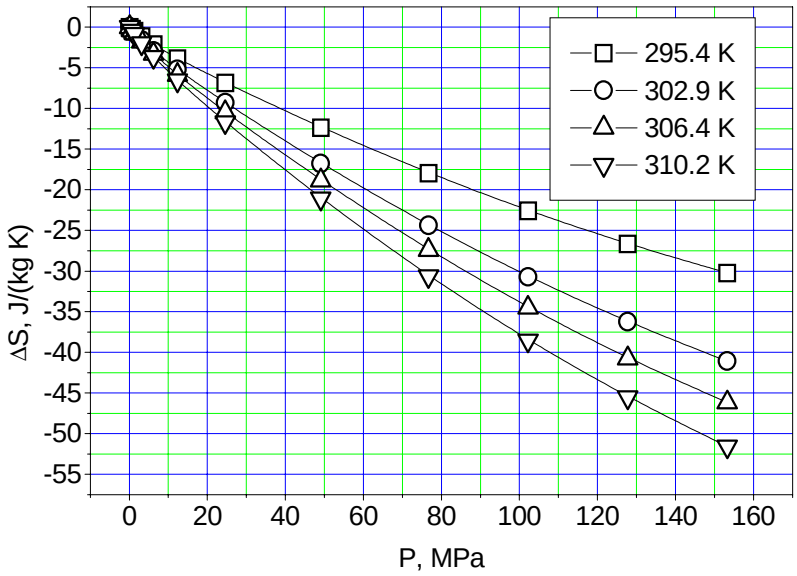
Fig. 2. Calculated energy (normalized to one molecule) of possible clusters in aqueous solution versus number of single molecules C_{60} entering them

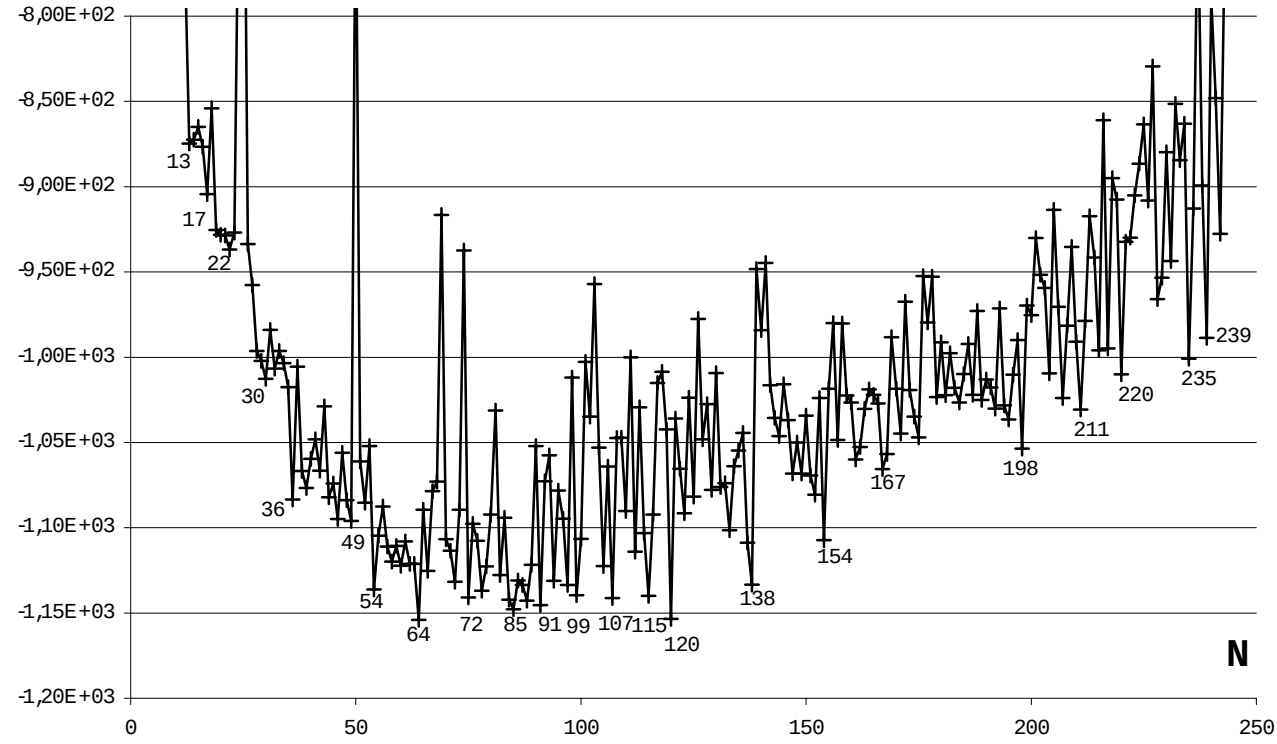
Fig. 3. Plot of weight-average molar mass M as a function of aggregation time for the prepared sample with concentration 1.1 $g \cdot l^{-1}$

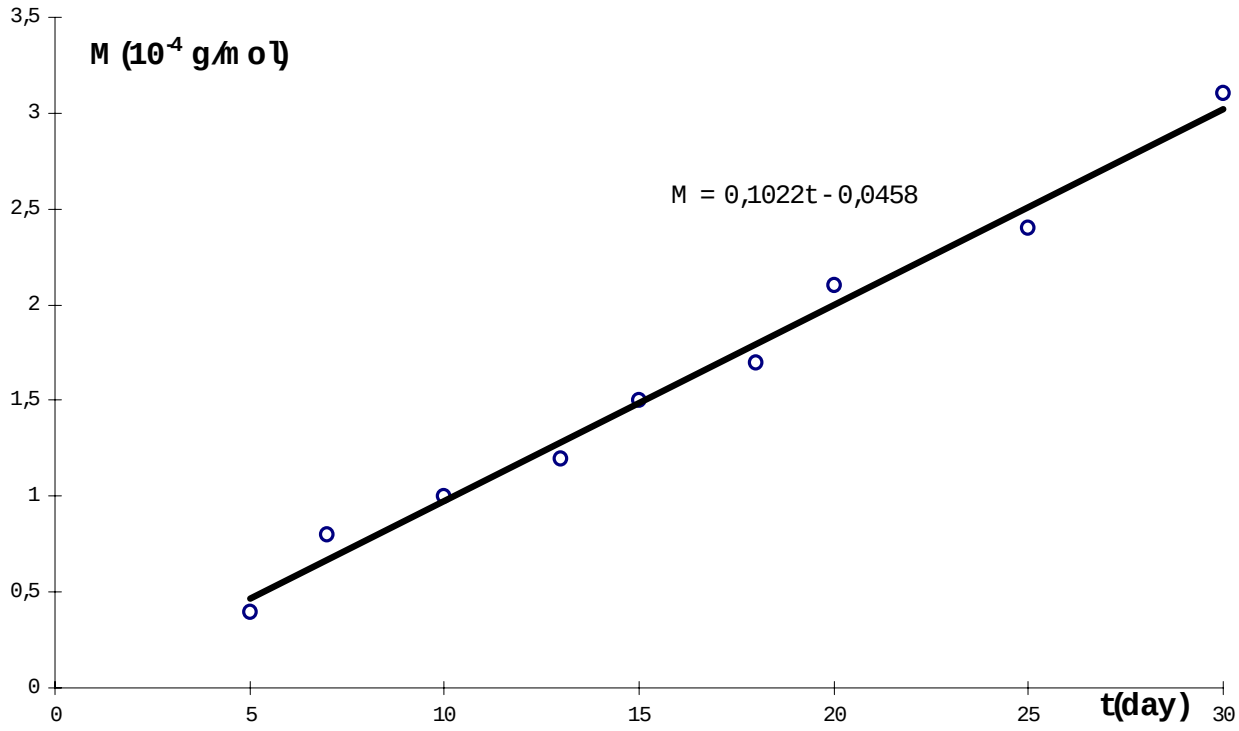
Fig. 4. The dependence of optical absorption coefficient of fullerene C_{60} aggregates in aqueous solution as a function of energy in the UV-VIS range

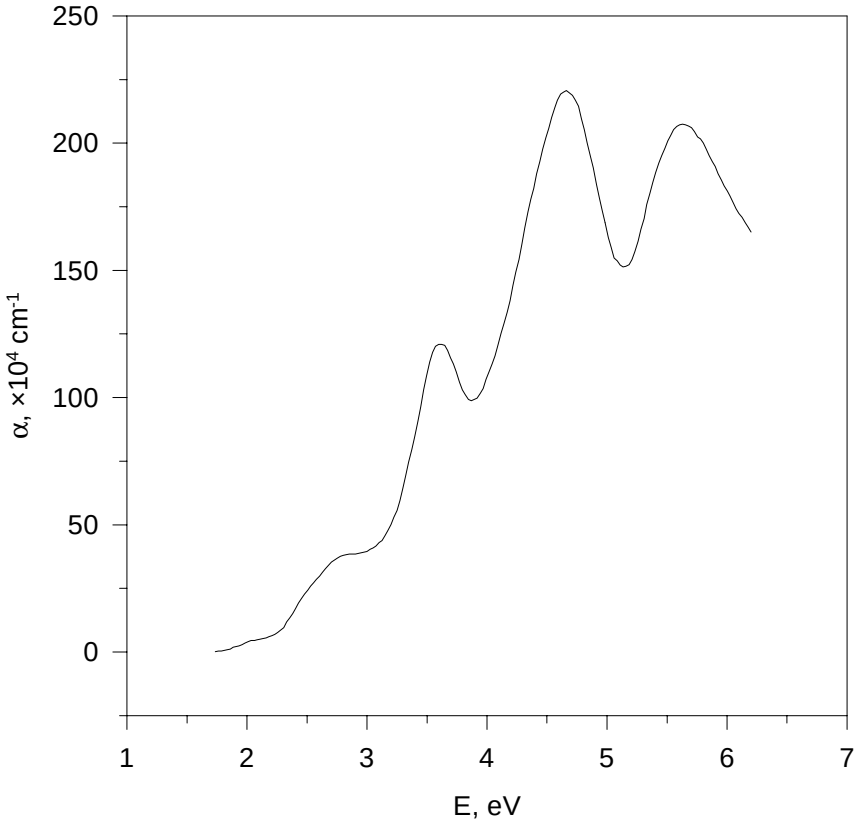
Fig. 5. The direct allowed transitions (•), indirect allowed transitions (◊) and indirect forbidden transitions (∇) in the fullerene C_{60} aggregates in aqueous solution in (2.1-3.0) eV range

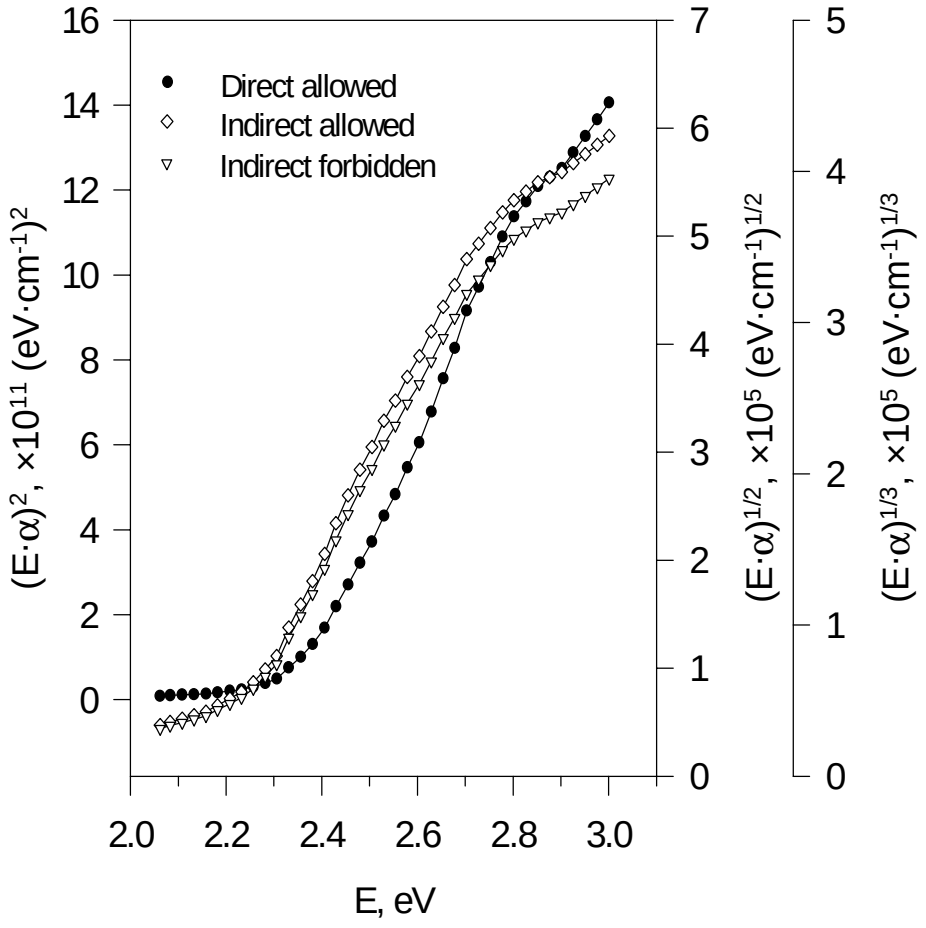
Fig. 6. The direct allowed transitions (•), indirect allowed transitions (◊) and indirect forbidden transitions (∇) in the fullerene C_{60} aggregates in aqueous solution in (2.9-3.7) eV range

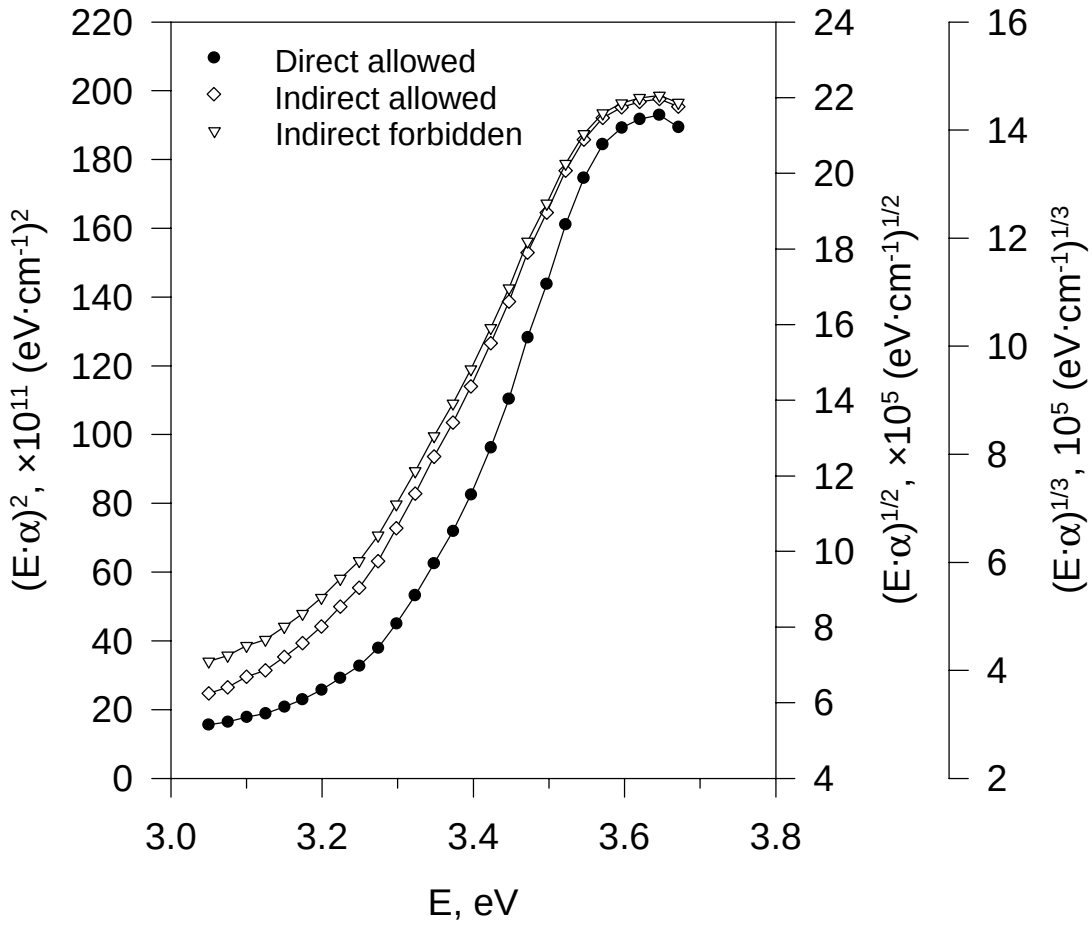

0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
ΔS, J/(kg K)
0
20
40
60
80
100
120
140
160
P, MPa
295.4 K
302.9 K
306.4 K
310.2 K


E/N (meV)
-8,00E+02
-8,50E+02
-9,00E+02
-9,50E+02
-1,00E+03
-1,05E+03
-1,10E+03
-1,15E+03
-1,20E+03
0
50
100
150
200
250
N
13
17
22
30
36
49
54
64
72
85
91
99
107
115
120
138
154
167
198
211
220
235
239


M (10-4 g/mol)
M = 0,1022t - 0,0458
t(day)
3,5
3
2,5
2
1,5
1
0,5
0
0
5
10
15
20
25
30


250
200
150
100
50
0
α, ×10⁴ cm⁻¹
1
2
3
4
5
6
7
E, eV


Direct allowed
Indirect allowed
Indirect forbidden
(E·α)², ×10¹¹ (eV·cm⁻¹)²
(E·α)^1/2, ×10⁵ (eV·cm⁻¹)^1/2
(E·α)^1/3, ×10⁵ (eV·cm⁻¹)^1/3
E, eV
16
14
12
10
8
6
4
2
0
7
6
5
4
3
2
1
0
5
4
3
2
1
0
2.0
2.2
2.4
2.6
2.8
3.0


Direct allowed
Indirect allowed
Indirect forbidden
(E·α)², ×10¹¹ (eV·cm⁻¹)²
(E·α)^1/2, ×10⁵ (eV·cm⁻¹)^1/2
(E·α)^1/3, 10⁵ (eV·cm⁻¹)^1/3
E, eV
0
20
40
60
80
100
120
140
160
180
200
220
4
6
8
10
12
14
16
18
20
22
24
2
4
6
8
10
12
14
16
3.0
3.2
3.4
3.6
3.8